



# Utilization of critical fluids in processing semiconductors and their related materials

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## Abstract

The use of carbon dioxide in its various states: supercritical (SC-CO<sub>2</sub>), liquid (L-CO<sub>2</sub>) or pellet form (snow-CO<sub>2</sub>) for processing and cleaning in semiconductor fabrication and related electronic devices is assessed in this review. An understanding of the fundamental mechanisms responsible for carbon dioxide-based processing, as in surface cleaning, is lacking. Although carbon dioxide is an excellent solvent for removing non-polar contaminants from a variety of surfaces, other CO<sub>2</sub>-based cleaning and surface modification processes are based on mechanical or morphological-induced changes in the interfacial region. The extremely low surface tension of CO<sub>2</sub> is a favorable property in terms of its rapid and complete removal from the substrate after a treatment has been affected, and this characteristic of CO<sub>2</sub> also accounts for its negligible effect on the morphology of the substrate, as utilized in the microelectronic industry. Applications of critical fluids in integrated circuit manufacturing operations, such as wafer cleaning, film deposition, photoresist stripping, drying, and particulate removal are noted.

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**Keywords:** Carbon dioxide; Cleaning; Critical fluid; Drying; Particulate removal; Photoresist; Semiconductors

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>)-based processes as utilized in semiconductor processing can incorporate several states or forms of CO<sub>2</sub>, such as SC-CO<sub>2</sub>, L-CO<sub>2</sub>, or the pelletized or CO<sub>2</sub> snow. Such processes are often employed in the cleaning of metal or electronic components, raw materials, or integrated circuits [1,2]. CO<sub>2</sub>-based processing is attractive because of its environmental compatibility and the fact that it supports a 'green' processing and sustainable technological platform [3,4]. These processes are of increasing importance in the semiconductor microchip industry where production of a 2-g microchip can consume 32 kg of water, 700 g of ultra-pure gases, 1.6 kg of fossil fuels, as well as 72 g of chemicals. For example, current techniques used in the production of baked-photoresists require the use of highly acidic or alkaline aqueous solutions and/or

organic solvents. The magnitude of such processing becomes even more apparent when one considers that a typical semiconductor plant might use up to 23,000 m<sup>3</sup>/day of water along with several cubic meters of organic solvents.

Weibel and Ober [5] have recently provided a review of SC-CO<sub>2</sub> use in microelectronics processing, while Mount et al. [6] have discussed the basic principles and benefits in employing SC-CO<sub>2</sub> for cleaning in this industry. In this review, basic mechanisms which contribute to the efficacy of CO<sub>2</sub>-based cleaning methods are described for the removal of organic contaminants, solid particulates, and deformable surface films or polymeric substrates, as occur in the photoresist development process. In the latter process, the various forms of CO<sub>2</sub> (SC-CO<sub>2</sub>, L-CO<sub>2</sub>, and CO<sub>2</sub> snow) have the potential to remove the photoresist, post-ash products, etchants, and chemical polishing residues (CMPs). Recent literature has been cited to demonstrate the use or potential application of critical fluids in the semiconductor industry however an emphasis has been placed on techniques developed at the Los Alamos National Laboratory (LANL), due to our familiarity with them, and the fact that many have not been described in the

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open literature. These include both basic and applied studies related to cleaning, photoresist stripping, and particulate removal.

## 2. Basic concepts

The advantage in using a critical fluid rests in the manipulation of its physicochemical properties, such as density ( $\rho$ ) and viscosity ( $\eta$ ), simply by varying pressure ( $P$ ) and temperature ( $T$ ). Such alterations in the fluid's thermodynamic and mass transfer properties allow the fluid to function as either a densified gas, a supercritical fluid, a liquid fluid, or a solid depending on the chosen  $P$  or  $T$ . The various fluid states can be represented as surface plane in three dimensions (Fig. 1a) that shows the interdependence of  $P$ – $T$ – $\rho$  for  $\text{CO}_2$ ; the fluid most is most often in the various applications we will discuss later. These above parameters in turn influence the solvation properties of the fluid and mass transport properties, such as  $\eta$ , as depicted in Fig. 1b which are important in the applications to be discussed later in this review. Ultimately, one is concerned with the development of high flux rate for the removal or addition of components via the use of critical fluids, and the flux rate is directly affected by both the thermodynamic and mass transport properties of the fluid.

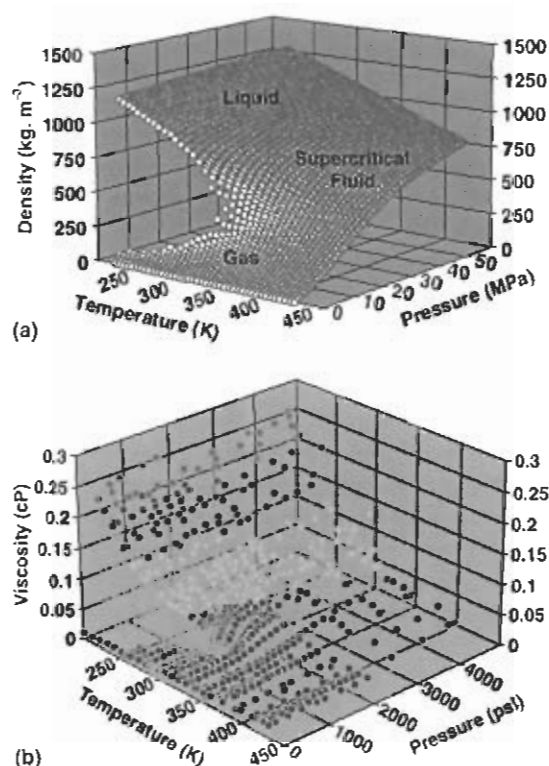


Fig. 1. Variation in fluid state as a function of the physicochemical properties of  $\text{CO}_2$ : (a) density and (b) viscosity (1 psi = 6895 Pa).

### 2.1. Ablative-based processing

Mechanical ablation or removal of particulates and contaminants on surfaces with  $\text{CO}_2$  is governed by a complex array of factors that include van der Waals and electrostatic interactions, drag and lift forces, and phase changes that occur when the  $\text{CO}_2$  molecule impacts on the surface. Ultimately particle removal from surfaces is dependent on the  $\eta$  and  $\rho$  of SC- $\text{CO}_2$ , two factors which impact on the hydrodynamics of the boundary layer which occurs at the fluid–surface interface. Theoretical calculations show that the boundary layer is a parabolic function of the  $\text{CO}_2$  velocity (Fig. 2), and exhibits only a weak dependence on temperature. It is these factors which determine the size of the particulates that can be removed with the various forms of  $\text{CO}_2$ .

Cleaning with  $\text{CO}_2$  involves several discrete mechanisms often acting in concert to achieve the final end effect. Removal of particulate matter by the process of abrasion or ablation, perhaps accompanied by solvation involves dynamics of the cryogenically developed  $\text{CO}_2$  particle and its interaction with the surface boundary layer. Upon ejection from a specially designed nozzle orifice,  $\text{CO}_2$  can exist in both a solid and fluid forms. The subsequent cleaning of the surface involves: (1) impact momentum of the  $\text{CO}_2$  particles to overcome the force of adhesional binding of the particle to the surface, (2) using the drag force of  $\text{CO}_2$  to remove particles from the surface, and (3) and possible dissolution of the particle into fluid  $\text{CO}_2$ . The velocity of the cryogenic  $\text{CO}_2$  particle decreases by 36% of its initial velocity over one relaxation time to cross the boundary layer. This relaxation time increases for larger particles of  $\text{CO}_2$ , indicating that they cross the boundary layer with an even larger velocity. The relaxation time also decreases with an increase in the  $\eta$  of the  $\text{CO}_2$  flowing over the surface, hence increasing the drag force experienced by the cryogenic particles of  $\text{CO}_2$  in the boundary layer.

From a practical point of view, adhesion forces governing effective removal of particles from surfaces

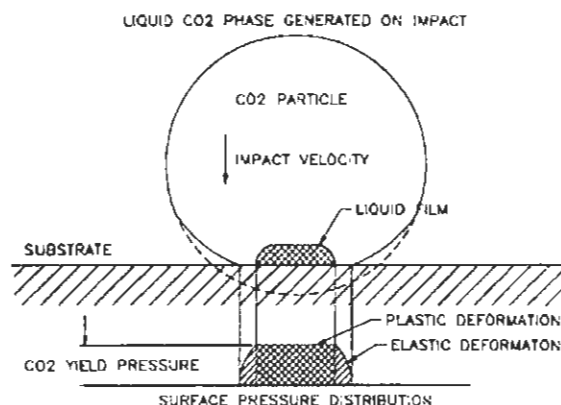


Fig. 2. Suggested  $\text{CO}_2$  'snow' cleaning mechanism.

have been discussed by Busnaina [7] and Matthews and Becnel [8]. Space does not permit a thorough discussion of the contribution of the seven basic adhesion forces governing particle removal, but an elegant discussion is available in a LANL report [9] available to the public at [www.scrub.lanl.gov](http://www.scrub.lanl.gov). Analysis of these forces that govern adhesion for a SiO<sub>2</sub> particle being removed by either L-CO<sub>2</sub> or SC-CO<sub>2</sub> from a silica surface versus those governing the dynamics of an identical particle–surface with water, indicate that additional force must be generated for the case of a dense phase based-CO<sub>2</sub> cleaning processes versus those available during aqueous-based cleaning. These supplemental forces for the CO<sub>2</sub> cleaning can be generated increasing the shear flow by applying higher CO<sub>2</sub> flow rates, through mechanical agitation or rastering of the substrate, or application of other force fields.

Further edification on the dynamics of particle removal has been described by Chitanvis et al. [10] and more recently Toscano and Ahmadi [11]. The key concept in their analysis is a mathematical description of the discrete regions of the attendant boundary layer undergoing impact with a cryogenic CO<sub>2</sub> particle. Coupled with the mathematical formalism of the contributing forces of adhesion or de-adhesion, along with CO<sub>2</sub>  $\rho$  and  $\eta$  data as a function of  $T$ , it is possible to determine the thickness of such a boundary layer as an inverse function of the velocity of the CO<sub>2</sub> impinging on the substrate surface. From this dependence, the radius of the smallest particle that can be detached from a surface as a function of the impingement velocity and temperature can be estimated. In general, operation at a lower temperature is more efficient, e.g., using SC-CO<sub>2</sub> at 300 bar and between 325–375 °K and a turbulent flow of 100–200 cm/s will permit removal of particles down to 0.1  $\mu\text{m}$ . This translates into delivering SC-CO<sub>2</sub> flows in the range of 30–60 l/min.

Carbon dioxide snow gun cleaning can also be applied to deformable film contamination on surfaces, i.e., organic contaminants, as noted in Fig. 2. Here the impact of cryogenically generated CO<sub>2</sub> particle deforms the contaminant film, distributing the surface forces which aid in film removal. Results generated at LANL's Supercritical Fluid Facility and elsewhere have shown that SC- and L-CO<sub>2</sub> cleaning of films of oils, greases, as well as model sorbates can be highly effective, and meet a 10  $\mu\text{g}/\text{cm}^2$  contaminant removal level associated with 'precision' cleaning. However a bias in cleaning effectiveness can exist that is dependent on the contaminant (sorbate)–substrate (sorbent) interaction; therefore each individual situation requires experimental verification.

## 2.2. Sorptive-based processing

The removal of polymeric films such as those utilized in photoresist development processes can be somewhat

more difficult than some of the previously cited examples. L- and SC-CO<sub>2</sub> interaction with polymeric substrates can produce several effects which facilitate cleaning, or could perhaps better described as 'debonding' of the polymer from the base substrate. Unlike the case of the deformable or soluble organic films noted previously, solubility of polymeric films in the various forms of CO<sub>2</sub> is limited, except at very high pressures [12]. However imbibition of SC- or L-CO<sub>2</sub> into polymeric films is well known [13–15] and can result in one of several effects, such as swelling, crystallization (or recrystallization), and selective extraction. These effects may aid in the removal of the film by the following means: (1) dissolution of CO<sub>2</sub> in polymeric matrix will swell the polymer, particularly if the polymer is held slightly above its glass transition ( $T_g$ ), but below its melt temperature ( $T_m$ ), (2) swelling of the polymer reduces the polymer–polymer interactions, lowering the overall solubility parameter ( $\delta$ ) of the polymeric film, and (3) swelling of the polymer reduces the polymer–substrate interactions, promoting debonding. A flow sheet summary of potential applications requiring polymer solubility in supercritical fluids and applications requiring supercritical fluid solubility in the polymer is shown in Fig. 3. Table 1 tabulates experimental measurements of CO<sub>2</sub> solubility in various polymers.

Photoresist stripping with CO<sub>2</sub>-based agents can be facilitated by adjusting operational parameters. As will be illustrated in a later section, the addition of a small amount of co-solvent into the SC-CO<sub>2</sub> can further induce swelling and debonding. Pneumatic pulsing of the CO<sub>2</sub> accompanied by defined rastering of CO<sub>2</sub> jet accentuates the above effects, resulting in a shattering of the polymeric coating and its physical removal, even in high aspect ratio configurations. It is also best to operate above the  $T_g$  (if known) for the polymeric film to imbibe more CO<sub>2</sub> which facilitates swelling of the polymer. By contrast, CO<sub>2</sub>-based cleaning of surface films exhibiting low or negligible solubility in SC-CO<sub>2</sub> requires a different mechanistic or theoretical treatment as well as experimental confirmation.

Application of adhesion science principles using such parameters as Hamaker constants or multi-dimensional solubility parameters ( $\delta$ ) can be used to qualitatively explain the ability of SC-CO<sub>2</sub> or snow-CO<sub>2</sub> to remove some surface films. Toward this end, the dissertation of Williams [16] elegantly describes the use of the  $\delta$  concept for optimizing conditions for polymeric film removal.

## 3. Applications of critical fluids

There are a plethora of applications of critical fluids related to semiconductor processing and related materials. It is impossible within the length of this review to cover all possibilities, but we have cited typical

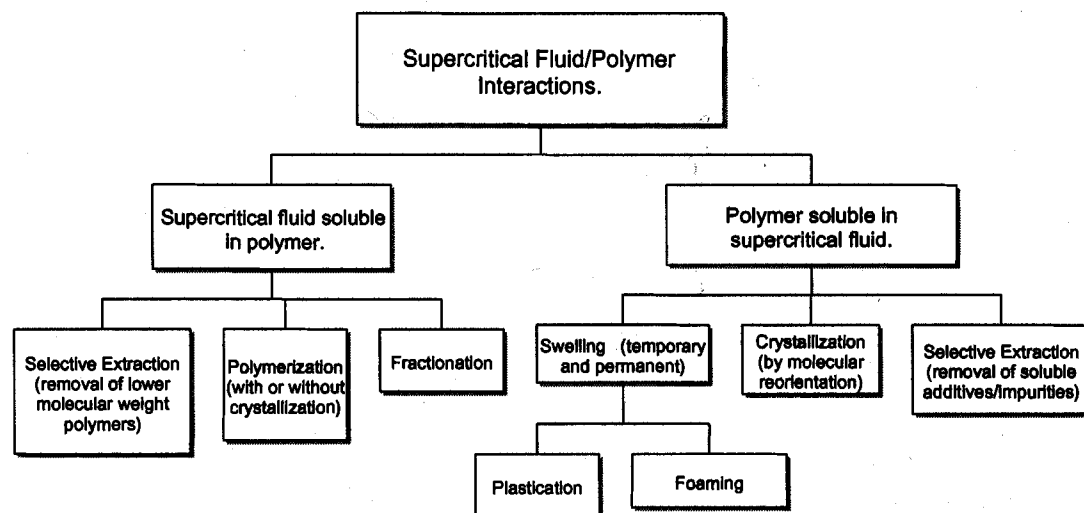


Fig. 3. Possible critical fluid–polymer interactions.

Table 1  
Experimental CO<sub>2</sub> solubilities in various polymers

Polymer	Approximate density (g/cm <sup>3</sup> )	CO <sub>2</sub> conditions of pressure and temperature	Sorption of [CO <sub>2</sub> ] (moles CO <sub>2</sub> /cm <sup>3</sup> polymer) × 10 <sup>-3</sup>	Reference
PMMA	1.19–1.26	20.7 MPa, 40 °C	3.53	[12]
ABS	1.04–1.06	20.7 MPa, 40 °C	1.75	[12]
HIPS	1.04–1.09	20.7 MPa, 40 °C	1.07	[12]
PPO	1.0–1.07	20.7 MPa, 40 °C	0.32	[12]
PET	1.38–1.41	20.7 MPa, 40 °C	0.55	[13]
PVC	1.38–1.41	20.7 MPa, 40 °C	0.48	[12]
PET	1.38–1.41	6.3 MPa, 35 °C	2.19	[14]
PVC	1.38–1.41	6.3 MPa, 35 °C	2.49	[15]
LDPE	0.89–0.93	20.7 MPa, 70 °C	0.17	[13]
PP	0.85–0.92	20.7 MPa, 70 °C	0.04	[13]

applications and developments which seem to hold promise, and given some specific examples from our research at LANL. In this section we shall focus on cleaning operations involving the various forms of CO<sub>2</sub>, deposition of films, photoresist development and removal, drying—particularly as related to MEMS, and particle removal.

### 3.1. Cleaning

Cleaning is a unit operation seminal to the semiconductor industry, ranging from improving raw material specifications (such as the cleaning of bulk silicon) to the high standards applied in chip manufacture. Bowling et al. [17] have summarized the challenges for cleaning in the microelectronics industry, while Bok et al. [18] critique the use of supercritical fluids in wafer cleaning. The zero surface tension exhibited by CO<sub>2</sub> provides a significant advantage over liquid and aqueous-based cleaning agents particularly with respect to cleaning high aspect ratio features. In general both the pulsed static and dy-

namic flow treatments methods have found applications, but the use of pressure pulsation and small quantities of co-solvents are generic to many of the described methods. Surface analysis suggests that SC-CO<sub>2</sub> cleaning removes contamination at a level equivalent to 1–10 monolayers, certainly below the level of 10 µg/cm<sup>2</sup>, which is a criterion for precision cleaning of most surfaces.

CO<sub>2</sub>-based cleaning will undoubtedly increase in use as the critical dimensions of integrated circuits are reduced, due to problems in using water or organic based solvents for accessing the trenches and vias. Wang et al. [19] verified the above postulate and offered a theoretical explanation to describe the flux rate of impurity removal from the target surface. A linear relationship was found between the degree of impurity removal and the applied fluid flow rate in a dynamic flow system. Sehgal et al. [20] noted the need to use polar co-solvents along with SC-CO<sub>2</sub> for the removal of higher molecular weight organic compounds from the via structures. Sputter and Hess [21] have provided further guidance with respect to optimizing the wetting through fluid transport of

nanoscale thin-film structures, noting that this is a diffusion-dominated transport mechanism, a factor favoring the use of critical fluid media. Experience with numerous substrates in our laboratory at LANL have verified that CO<sub>2</sub>-based critical fluid methods do not damage the supporting substrates, and this has been verified by the studies of O'Murchu et al. [22].

Numerous applications abound, e.g., post-plasma-etch residues have been successfully removed using CO<sub>2</sub>-based fluids. Myneni and Hess [23] comment that use of CO<sub>2</sub> prevents 'pH shock', thereby reducing metallic corrosion as well as the need to apply an isopropanol rinse step to remove water from the semiconductor chip. Korzenski et al. at Advanced Materials Technology have effectively applied SC-CO<sub>2</sub> for the following: (a) silicon nitride particle removal from patterned Si/SiO<sub>2</sub> surfaces, (b) ashed and non-ashed aluminum post-etch residue removal, and photoresist and ion-implanted photoresist removal [24]. It is also particularly gratifying to see SC-CO<sub>2</sub> being applied to ultra-low-*k* materials [25,26].

A host of devices and formulation have been invented or applied for cleaning in the integrated circuit industry. Typical is the use of surfactants, chelating agents, or reactive chemicals imbibed in CO<sub>2</sub> as cited in the patent application of Xu et al. [27], and such mixtures are often used effectively without maintaining a single phase. Even water or ozone has been applied in conjunction with pressurized CO<sub>2</sub> [28,29] to provide a more aggressive environment for cleaning surfaces. Typical unit operation equipment, including 'cluster' tools for cleaning have been described by Perrut et al. [30], DeSimone et al. [31], and Bok et al. [18] in the literature.

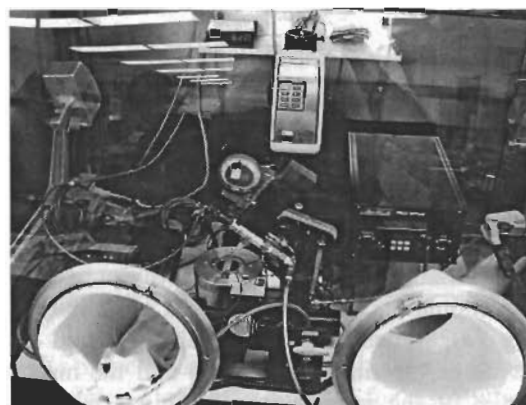


Fig. 4. VA-TRAN 'snow' gun apparatus in a glove box.

Pelletized or snow gun CO<sub>2</sub> also finds application in the integrated circuit industry [32]. Typical snow gun results obtained on a LANL-modified VAN-TRAN apparatus (Fig. 4) are shown in Table 2 for the removal of Apiezon N grease from a substrate. The experimental parameters examined included a nozzle angle variance of 60–80°, a nozzle distance from substrate of 4 mm to 2.5 cm, a 10 min total processing time, and a delivery pressure of 5.5 MPa. These results were optimized using a commercially available low pressure nozzle as opposed to the higher pressure option. As can be seen in Table 2, the most promising results corresponded to those in shaded portion of the Table 2. Snow gun cleaning effectiveness is somewhat dependent on the identity of the nature of the contaminant, e.g., a lubricating oil or Apiezon N appear to be more easily removed, while silicone oil films are more resistant to snow gun cleaning.

Table 2

Contamination levels before/after automated snow gun cleaning of Apiezon N contamination

Residue analysis		CO <sub>2</sub> snow gun parameters		
Amount of contaminate (μg/cm <sup>2</sup> )	Amount of residue (μg/cm <sup>2</sup> )**	Number of passes*	Nozzle distance to target	Nozzle angle by degrees
250	88.2	4	2.5 cm	80
250	102.9	4	1 cm	56
250	127.9	4	1 cm	68
250	80.7	2	2.5 cm	80
125	20.8	2	1.0 cm	80
250	30.6	3	1.0 cm	80
250	25.0	3	2.5 cm	80
125	22.2	2	2.5 cm	80
250	30.2	2	4 mm	70
250	34.2	5	4 mm	70
250	10.5	4	2.5 cm	70
125	~1.4	4	2.5 cm	60
125	12.5	4	2.5 cm	60
250	12.5	4	2.5 cm	60
250	11.1	6	2.5 cm	60
250	22.2	6	2.5 cm	60
250	23.6	6	2.5 cm	60
250	<5	TCE cleaned		
125	<5	TCE cleaned		

### 3.2. Photoresists

The development, deposition, and removal of photoresists have been a major application focus of the critical fluid technology platform. Again, successful application of these approaches is dependent on developing or preventing collapse of the photoresist pattern. Jincaco et al. [33] have theoretically treated this problem and note that the relative size of the actual pattern spacing should exceed the minimum allowable pattern spacing ( $d$ ), which can be calculated based on the properties of the rinse fluid ( $\text{CO}_2$ ) and the mechanical properties of the resist material. This is important in memory base applications as the information density increases with a decrease in the spacing critical dimension.

With respect to the properties of the resist material, investigators have been developing specialized polymers with enhanced solubility in L- and SC- $\text{CO}_2$  as an aid in lithography process. Typical are the studies reported by the Cornell group of Ober [34–36] in which fluoromethacrylate block copolymers are custom designed to enhance their solubility in a compressed  $\text{CO}_2$  medium. This allows E-beam patterning between 150–200 nm to be achieved and consequently the development of an ‘all dry’ lithography process. A similar approach has been taken by DeSimone et al. [37] for the development of acrylate polymers with enhanced solubility in  $\text{CO}_2$  for their use as lubricants in disk drives. Again as in cleaning processes described in the last section, compatibility of the SC- $\text{CO}_2$  stripping process with substrate materials must be assured. Millet et al. in France [38] have recently shown that  $\text{CO}_2$ -based photoresist removal is compatible with attendant pressure cycling that is often applied for porous low- $k$  materials and copper. Even mixtures of water with  $\text{CO}_2$  have been shown to be beneficial in the photoresist removal process [39] with no adverse effect, especially for low- $k$  materials exhibiting limited solubility in  $\text{CO}_2$  and having very high  $T_g$ 's.

As remarked previously, neat  $\text{CO}_2$  is not sufficient to remove most photoresists. The use of a minimal amount of environmentally benign co-solvent along with pressure fluctuation to induce film breakup are standard operating parameters for stripping photoresists. Such an approach has been used by various groups including You in South Korea [40] and Biberger at Supercritical Systems, Inc. [41]. This is the basis of the LANL-developed SCORR process [42–44] which will be described in greater detail below.

Using the patented LANL-SCORR (supercritical  $\text{CO}_2$  resist removal) process as an example, the effects of  $\text{CO}_2$  and incorporation of a co-solvent on the removal of the masking polymeric films can be demonstrated. The above process is enhanced by ablative-based pulsing and rastering of the  $\text{CO}_2$ -cleaning agent across the substrate surface at a specific delivery angle. Elastic

deformation of the polymeric film under the above conditions occurs most readily at temperatures slightly above the glass transition,  $T_g$ , of the polymer.

Studies on Si/Al wafers with respect to photoresist stripping illustrate the effectiveness of a SC- $\text{CO}_2$  cleaning process. Results from surface characterization studies such as FTIR, SEM, Auger and nuclear reaction analysis (NRA) confirm the efficacy of  $\text{CO}_2$ /co-solvent pressure pulsing tandem as an effective way to clean and strip the photoresist, even in the ‘trench’ profiles [42]. In a specific case, samples of GaAs and GaP wafers covered with positive (AZ-4330) photoresist, as well as Si wafer samples with Al, Ti–Pt, Ti–W and In–Sn oxide metallizations covered with the same positive photoresist were treated via the SCORR process using SC- $\text{CO}_2$ . These 1/2-in. square samples were treated on a SCORR system consisting of a compressed gas cylinder feeding into a high pressure syringe pump that supplies high-pressure, but ambient-temperature SC- $\text{CO}_2$  into a ballast tank and eventually the treatment vessel (Fig. 5). The 1/2-in. square sample is then centrally mounted inside the treatment vessel. The initial conditions for the ballast tank and treatment vessel are 11 MPa and 50 °C and 7.6 MPa and 50 °C, respectively. Pulsing of the  $\text{CO}_2$  pressure is achieved by changing the pressures in the ballast tank and treatment vessel over the quoted ranges. This is accomplished approximately three times along with applying 5 vol% propylene carbonate ( $\text{PCO}_3$ ) during the pulsation cycle. Finally, the  $\text{PCO}_3$  is shut off, and a pure  $\text{CO}_2$  ‘rinse and dry’ step applied to the treated sample to remove all of the  $\text{PCO}_3$  particulate material. The sample is then removed from the treatment vessel and analyzed for the presence of residual photoresist using NRA.

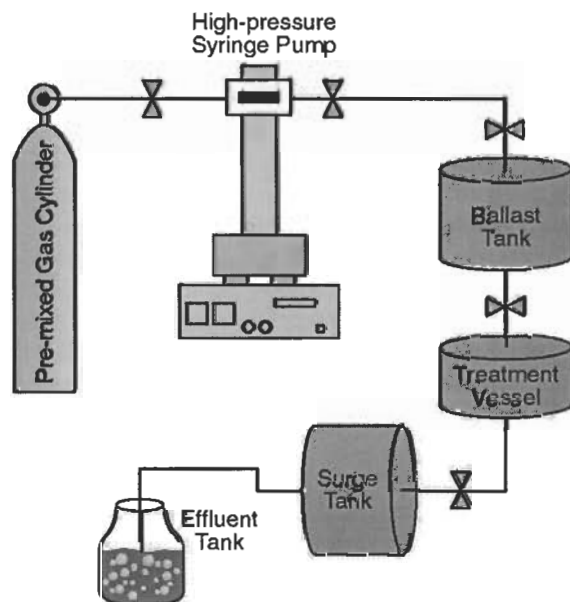


Fig. 5. Experimental apparatus for photoresist stripping.

Table 3

NRA surface analysis results for Si-metallization systems treated by a SC-CO<sub>2</sub>-based cleaning process (SCORR)

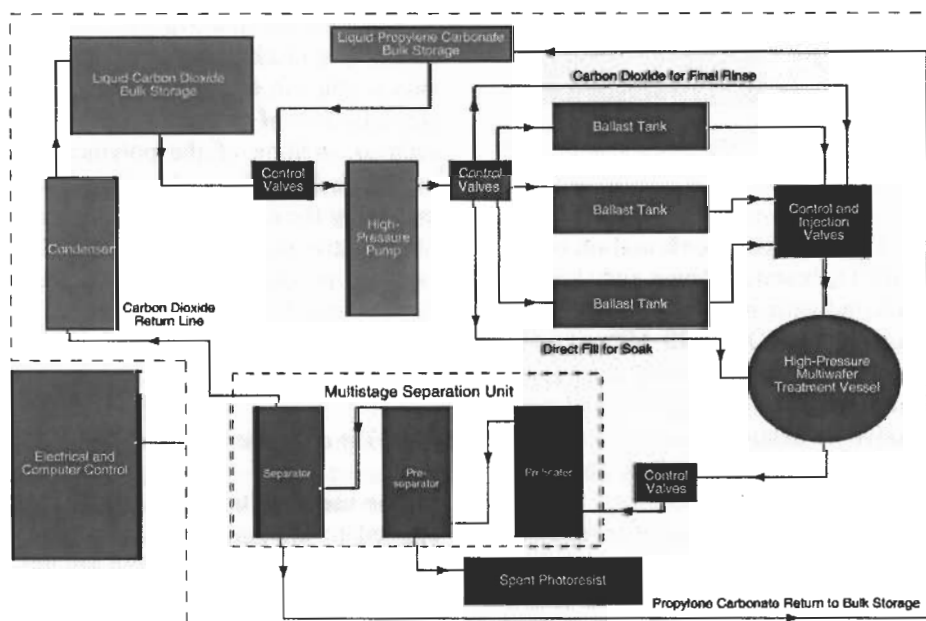
Sample description	Experimental gross yield, $Y$ (counts)	Experimental background (counts)	Adjusted yield, $Y^{1,2}$ (counts)	( $nt$ ) (C-atoms/cm <sup>2</sup> )	Equivalent conc. of surface carbon atoms
Al film on Si	189	8	$116 \pm 14$	$(1.0 \pm 14) \times 10^{16}$	10 monolayers
Al film on Si	194	24	$105 \pm 15$	$(9.3 \pm 13) \times 10^{15}$	
In-Si oxide film on Si	13.8	7	$66 \pm 12$	$(5.9 \pm 1.1) \times 10^{15}$	6 monolayers
Ti/W film on Si	97	5	$27 \pm 4$	$(2.4 \pm 0.4) \times 10^{15}$	2 monolayers
Ti/W film on Si	159	4	—	—	—
Pt/Ti film on Si	74	6	$3 \pm 4$	$(2.7 \pm 3.6) \times 10^{14}$	1/3 monolayers

Column 2 in Table 3 gives the experimental proton yield from the NRA analysis of residual C on the surface on the listed samples. As indicated in Table 3, each sample analyzed by NRA analysis must have an experimental background and adjusted proton count applied to eventually yield the C-atoms/cm<sup>2</sup> on the surface of the CO<sub>2</sub>-treated specimens (column 5—Table 3). These surface concentrations of C-atoms divided by the approximate value for a monolayer of C-atoms on a surface ( $1 \times 10^{15}$  C-atoms/cm<sup>2</sup>) yields the approximate number of monolayers of carbon atoms on the surfaces (column 6—Table 3), and hence the relative cleanliness of the surfaces after treatment with SC-CO<sub>2</sub>. These monolayer values indicate that a high degree of photoresist removal has been achieved, particularly for these test specimens that were cleaned in an open laboratory environment and not a clean room. In addition, the presence of residual adsorbed CO<sub>2</sub> left over from the cleaning process cannot be discounted.

A schematic of the scaled up process is illustrated in Fig. 6. Here the basic concept described above and illustrated by Fig. 5 has been transformed into an on-

line cyclic process. Liquid CO<sub>2</sub> is fed into a high pressure pump module as indicated in Fig. 6 for distribution into the ballast tanks. Through automated controlling of the valve sequence the pressure can be altered and PCO<sub>3</sub> added in a sequential fashion into the treatment vessel. A similar sequencing of valves are then used to feed the exhaust CO<sub>2</sub>-co-solvent mixture into the tandem vessel multi-stage separator unit after completion of the photoresist stripping operation. Here the residual photoresist is separated from the exhaust CO<sub>2</sub> and PCO<sub>3</sub> recovered before returning the CO<sub>2</sub> to the heat exchanger circuit and ultimately the pump feed.

Some additional examples of the effectiveness of SC-CO<sub>2</sub> surface cleaning on semiconductor photoresist surfaces are shown in the scanning electron microscopy (SEM) photomicrographs in Figs. 7 and 8. Fig. 7a shows an intermediate, partial strip of the polymeric photoresist by the SCORR process, while Fig. 7b shows that the photoresist and concomitant polymeric residue products are removed from the surface. Fig. 7c and d shows before/after SEM scans of a similar fluorinated residue stripped from the top of a photoresist via SC-CO<sub>2</sub> using

Fig. 6. On-line process photoresist removal scheme using CO<sub>2</sub>.



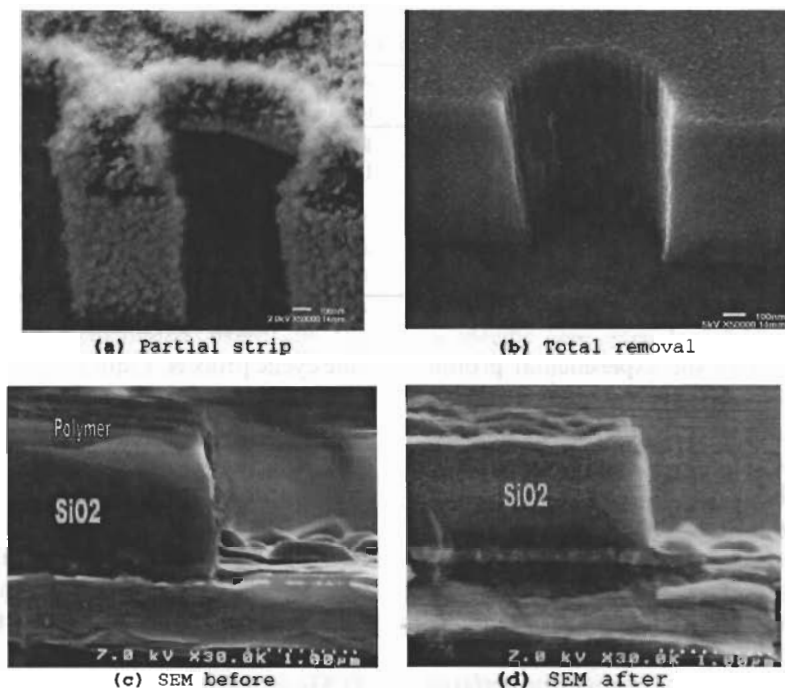


Fig. 7. SEM study of the removal of photoresist film using SC-CO<sub>2</sub> (SCORR process).

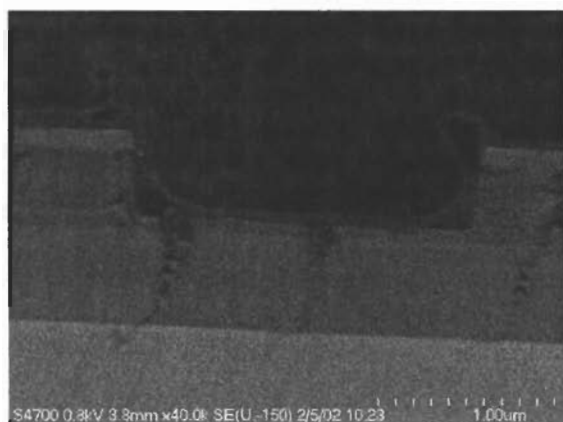


Fig. 8. Swelling and delaminating of polymer film in a trench of a semiconductor wafer induced by SC-CO<sub>2</sub>.

the SCORR process. This is further confirmation of the overall effectiveness of CO<sub>2</sub>-based stripping and cleaning as applied in the semiconductor industry. These results were achieved employing SC-CO<sub>2</sub> at 20 MPa, 85 °C, using either propylene or butylene carbonate as a co-solvent at 1.0–3.8 vol% concentrations. Such conditions have also proven effective for delaminating poly-(methyl-methacrylate) and Novalac resin from silica and Al/C surfaces.

Additional evidence of this effect is shown in the SEM photograph (Fig. 8) of a photoresist film that has undergone delamination after swelling in the trench of an etched silica wafer. This situation is best achieved using temperatures between the  $T_g$  and melting point of

the polymer composing the photoresist film. As noted previously, cleaning of semiconductor surfaces with CO<sub>2</sub> does not effect most metallic substrates studied to date, including low- $k$ , dual Damascene laminations that find extensive use in the semiconductor industry. Such success bodes well for further adoption of CO<sub>2</sub>-based removal processes in the semiconductor industry.

In summary, photoresist stripping via SC-CO<sub>2</sub> is optimized by using a co-solvent, rastering of the nozzle assembly over the target area, and a pulsed-flow system to dislodge and remove the surface film and contaminants. The mechanism by which the above process occurs is still not totally understood, but appears to be a combination of a number of physicochemical effects such as swelling of the polymer film, lowering of the polymer's  $T_g$ , and possible degradation of the polymeric matrix by the combined effects of pressure and presence of a reactive co-solvent. The role of film elasticity in the swelling of thin polymer films in density fluctuating supercritical fluids has been confirmed by Koga et al. [45] who invoke the concept similarly formulated by Williams [16].

### 3.3. Film deposition

The use of critical fluid media for film deposition as applied to integrated circuit processing is relative new and developments in the field are not necessarily totally directed towards the above goal. These range from fundamental studies of the reactions of organosilanes on silica surfaces in CO<sub>2</sub> [46] to the development of film



precursors that are volatile and soluble in pressurized CO<sub>2</sub>. Considerable fundamental research has been done on developing the appropriate reagents and conditions for both metallic as well as polymer film deposition, and a total review of work in this area is beyond our scope here.

Key investigators involved in this area, a generic description of their research objective, and a few select references are summarized below:

Wai and coworkers—CO<sub>2</sub> soluble chelates; metallic films on silicon and germanium substrates [47].

Sievers and coworkers—transport chemical deposition processes; Pd, Zr, etc. film formation [48,49].

Watkins and coworkers—Pd films on Si wafers and polyimide; hybrid technique for metallization, Cu deposition [50–53].

Kondah and Kato—Cu deposition from SC-CO<sub>2</sub> [54].

Of particular interest are the studies of the Gangopadhyay research group on the extraction of porogens to produce porous low-*k* film structures. Using specific polymers [55,56]. This group has produced low-*k* films whose values are consistently from 2–3; equivalent to those found via other processes. Similarly, using hexamethyldisilazane (HMDS)–SC-CO<sub>2</sub> mixtures, they have cured plasma-damaged nanoporous low-*k* films, restoring their hydrophobicity and dielectric properties after plasma treatment. Krause et al. [57] have used specially designed block copolymers to also produce low-*k* dielectrics via a foaming mechanism aided by the presence of CO<sub>2</sub>. These nanofoams have extended applications beyond just the semiconductor field.

Impregnation of metals into porous supports can be facilitated using the superior mass transport properties of SC-CO<sub>2</sub>. Howdle's group at Nottingham has reported impregnation of silver particles into porous polymer beads and silica aerogels [58]. Such a development has obvious potential and applicability in semiconductor integrated circuits. This approach has been incorporated by Homes and coworkers [59] to produce ultra-high density semiconducting nanowires on a chip, i.e., 10<sup>–12</sup> nanowires/cm<sup>2</sup> consisting of germanium on silicon and quartz substrates.

### 3.4. Drying and application to MEMS

Pressurized CO<sub>2</sub> has a small, but finite solubility for water over an extended range of temperatures and pressures [60]. This principle can be used to remove moisture from a number of materials, including microelectronic and microelectromechanical systems (MEMS). Like the technique of critical point drying that is used to prevent cellular collapse in biological specimens prepared for SEM analysis, both applica-

tions utilize the low surface tension forces exhibited by CO<sub>2</sub> on many substrates, to mitigate dehydration effects without deforming matrix morphology. Carbon dioxide can also be used for the removal of organic solvents (like isopropanol) from substrates, thereby serving as a displacement agent after the washing or rinsing of a microelectronics part with a designated solvent.

The above property of pressurized CO<sub>2</sub> is starting to be widely used in drying micro- and nano-structures to avoid perturbation of the desired structure or pattern. For example, Petricich et al. [61] have applied SC-CO<sub>2</sub> for drying high aspect ratio resist structures (60–70 nm line/space patterns occurring on 250 nm resists having 3.5–4.2 aspect ratios) that are utilized in conjunction with electron-beam projection lithography. In this case, no resist pattern collapse was recorded. Namatsu [62] has noted that water-rinsed resist patterns can be effectively dried with CO<sub>2</sub> provided a surfactant is integrated into the process. Two alternative techniques have been described; initially employing L-CO<sub>2</sub> in conjunction with either a fluorosurfactant in an organic liquid, or dissolving the surfactant directly into the L-CO<sub>2</sub>. Ultimately, the L-CO<sub>2</sub> is subsequently converted to its supercritical state to effect the drying operation which has successfully worked on resist having aspect ratios up to 7. A similar approach has also been reported by Goldfarb et al. [63] for drying APEX-E and UV6 resists.

Fundamental studies on nanostructures by Namatsu et al. [64] have demonstrated the clear superiority of SC-CO<sub>2</sub> drying over drying with nitrogen gas. This has encouraged the development of various types of CO<sub>2</sub>-based dryers for the microelectronics industry [65]. In general, it was found that by the increasing SC-CO<sub>2</sub> pressure, film thickness could be enhanced, commensurate with the enhanced removal of water from resist infrastructure. The water-removing properties of CO<sub>2</sub> have resulted in commercial dryer systems that can handle wafer sizes up to 6 in.

Of particular note, is the use of the above principle to remove water and other contaminants from MEMS-based devices. CO<sub>2</sub>-based drying helps prevent sticktion which often occurs in MEMS devices following their final release etch. Interesting studies at Sandia Laboratories [66] have verified the effectiveness of the CO<sub>2</sub>-based drying and cleaning on singly clamped cantilever beam components which are part of a microengine device. Details on the MEMS devices have been reported by the above group [66]. It was found that a combination of SC-CO<sub>2</sub>–methanol drying at 16 MPa and 35 °C worked very well resulting in an increasing in sticktion yield to 78%. This was a result of using CO<sub>2</sub>-drying which decreased the interfacial adhesional energy by three orders of magnitude, and subsequently increased the yield of microengines by a factor of 3.

#### 4. Conclusions

It is apparent from this above review and assessment, that the critical fluid technology platform utilizing compressed CO<sub>2</sub> can make a significantly contributions to the planned International Technology Roadmap for the Semiconductors Industry [67]. Here CO<sub>2</sub>-based cleaning processes are mentioned six times, lending credence to its adoption by industry. This is largely due to the fact that as critical dimensions and aspect ratios associated with improved performance of microelectronic devices decrease, it will become necessary to retain and fabricate at tolerance levels that are extremely precise. The availability of a fluid such as CO<sub>2</sub>, exhibits zero surface tension when interfaced with these very precise structures, suggests that it will see increasing use in the future, and lessen the industry's dependence on chemical solvents and water; ultimately improving the environment in the process.

As shown in Fig. 9, there are a number of patents which have been tendered in the various areas of application, and these have been plotted versus specific corporate assignees. From this data, one can see there is considerable industrial interest in applying critical fluids to the overall microelectronics fabrication process. This interest is shown not only by large end users, i.e., microelectronics corporations, but also by companies that supply processing equipment and gases. Among these firms are Kobe Steel, IBM, Texas Instruments, Tokyo Electron, Micell, Hughes Aircraft, Praxair, Air Products, and Dainippon Screen. Currently much of the

activity appears to be in the cleaning and etching of silicon wafers, but it is anticipated that the areas of drying, MEMS production, and low-*k* dielectric fabrication will see an increase use of the critical fluid technology platform.

Confidence in the technology is shown by the formation of several large consortia consisting of end users, equipment fabricators, gas suppliers, and specialty chemical firms who have combined to further advance the critical fluid-based processing platform in the semiconductor industry. For example, collaborations exist between the following organizations:

Dainippon Screen–Kobe Steel–Ashland Chemical–Samsung  
Tokyo Electron–Praxair–EKC  
BOC Edwards–Micell Integrated Systems  
Altis Semiconductor–Separex–Air Liquide–CEA  
IBM–SC Fluids–Air Products–ATMI

Commercially available processing modules are not available from several vendors. For snow gun-based cleaning, equipment can be provided by 10 different suppliers; a CO<sub>2</sub> drying module for MEMS application is offered by SC Fluids, and supercritical CO<sub>2</sub>-based processing systems are available from Supercritical Systems, Inc.—Accudyne Systems, Separex, and SC Fluids. The LANL-based SCORR process has initially been commercialized by SC Fluids, Inc. under the trade name, Arroyo, and several units have been sold to IBM. This automated turnkey system is configured as a cluster

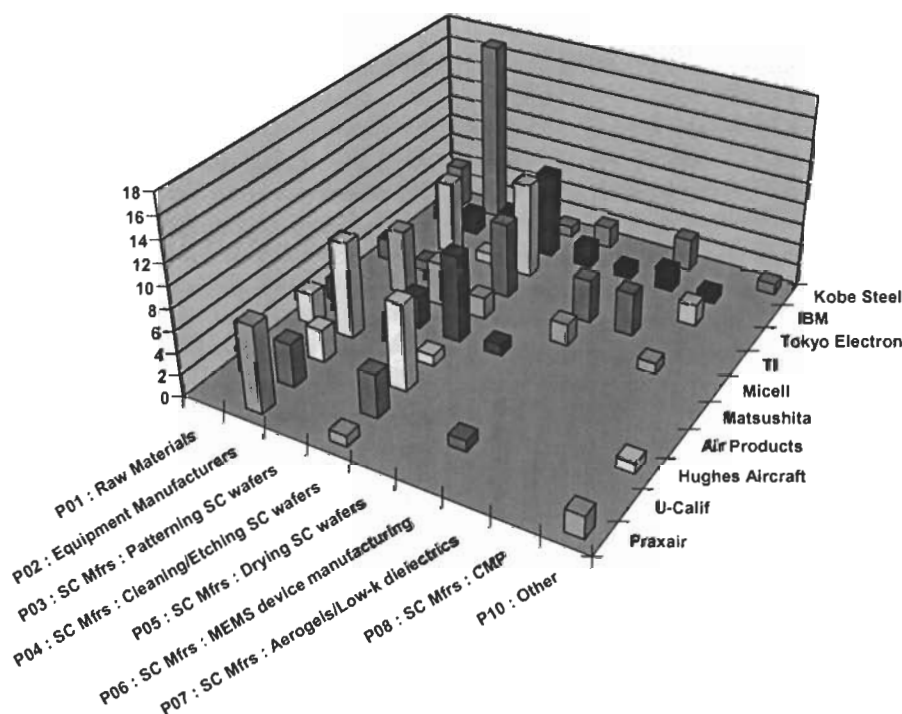


Fig. 9. Subject patent filings versus identified patent assignees.

tool, permitting modular addition for processing up to 50 in two 25—wafer lots (either 150 or 200 mm) stands as testimony to the arrival of critical fluid processing as a viable operation for the semiconductor industry.

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